

Electroactive Materials Composed of Starch

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Extruded films of plasticized starch were doped with metal halides to produce solid ion-conducting materials. The electrical conductance of the material increased from 10^{-11} to 10^{-6} Siemens/cm. The type and amount of dopant affects the conductance of the material. Although the materials are moisture sensitive, water content does not have a significant effect on the conductance of doped films. Mechanical properties of doped films indicate that the starch is plasticized and that the ion-conducting material is strong and tractable. Unlike intrinsically conductive polymers, electroactive starch materials can be extruded in thin films or molded into any shape.

KEY WORDS: Starch; conductance; polymeric material.

INTRODUCTION

Historically, polymers have functioned as insulators and dielectric materials [1], and they can be tailored to exhibit specific mechanical properties. Generally, solid polymer electrolytes have conductivities around $1 \text{ S/cm} > \sigma > 10^{-4} \text{ s/cm}$. Ion-conducting polymers are different from organic, intrinsically conducting polymers such as polypyrrole, polyacetylene, polythiophene, polyphosphene, and polyaniline [2,3]. The range of conductivity for intrinsically conducting polymers is 10^{-6} to 10^4 S/cm . Conducting organic polymers are usually prepared in the form of intractable films, gels, or powders that are insoluble in most solvents. Others are cast out of acidic aqueous or nonaqueous solvents such as ether. To increase or modify the electrical properties of conductive polymers, they can be doped with various salts [4]. The instability of some conductive polymers is directly related to the physical morphology. For most conductive

polymers, it is not possible to manufacture formed parts by means of a molding or extrusion process.

Starch is a biodegradable, renewable resource and is composed of a mixture of linear and branched polysaccharides. Amylose is a linear polymer of (1,4) linked anhydroglucose units (AGU). Amylopectin is a highly branched polysaccharide composed of linear (1,4) AGU chains, with branch points being (1,6) linkages. Although starch is packaged into granules in its native state, the properties of starch materials are exhibited when the granular structure is broken down by mechanical and thermal means. The characterization of the electrical properties of starch-based materials was first performed during the development of inherently antistatic, biodegradable, starch-based loose-fill packing materials at NCAUR [5]. In recent literature, ion dissociation in plasticized polysaccharides has been shown to affect conductivity for amylopectin-rich starch [6] and chitosan [7].

Electrically conductive polymers based on starch or other renewable resources would be useful for energy storage and electromagnetic shielding applications.

EXPERIMENTAL

Materials

Commercially available cornstarch (Buffalo 3401, CPC International) with an ambient moisture content of approximately 10% was used. Samples were extruded by

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Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that also may be suitable.

a Brabender single screw (3:1 high shear mixing zone) extruder with four heating zones (three barrel, one die). The barrel temperature profile was 130°C–150°C–150°C. Samples were extruded with an adjustable thickness sheet die with a width of 4 inches. The temperature range of the die varied from 90°C to 120°C depending on the water content of the sample. In general, samples containing a high water content needed lower die temperatures to prevent foaming. All samples were conditioned for at least 24 h at 50% relative humidity and room temperature before testing.

Methods

An Ohaus Moisture Balance (Florham Park, NJ) was used to determine the moisture content (MC) of the starch products by gravimetric methods. Samples were heated for 20 min at 110°C. Electrical resistivity was measured at room temperature using a Keithley constant current source (Model 487 picoammeter, Electro Tech Systems, Glenside, PA) with a concentric electrode system (ETS Model 803b). This test method conforms to the standards established by ASTM D257 and ESD S11.11 and involves a direct-current (DC) procedure for surface and volume resistance and resistivity of powders, pellets, and thin sheets. The resistance is measured using a defined electrode configuration, test voltage, and environmental conditions. Data was recorded by custom software. Conductance (σ) in Siemens/cm (S/cm) was calculated by

$$\sigma = \frac{1}{R_v} \quad (1)$$

where R_v is the volume resistance of the sample. For clarity on plots, the logarithm of the conductance is reported.

RESULTS

We investigated the structure–function relationships in starch-based ion-conductive materials [8]. In starch-based materials, there is a correlation between the moisture content and conductivity [9,10]. Water, however, is insufficient to account for the increase in conductivity of doped starch-based materials. Doping starch-based materials with M^+X^- resulted in an increase in conductance above that which could be attributed to water in the sample (Fig. 1).

The conductance of a material is expressed by

$$\sigma(T) = \sum n_i q_i \mu_i \quad (2)$$

where σ is the conductance of the material at a certain temperature (T), n is the number of charge species per

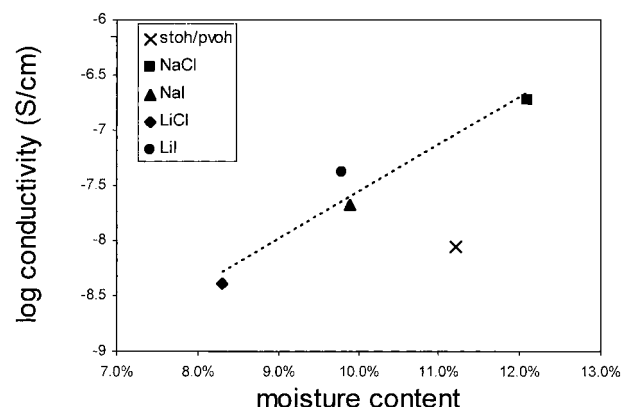


Fig. 1. Conductance and moisture content of thermoplastic starch doped with metal halides. The salt concentration is approximately 11% w/w of the dry blend.

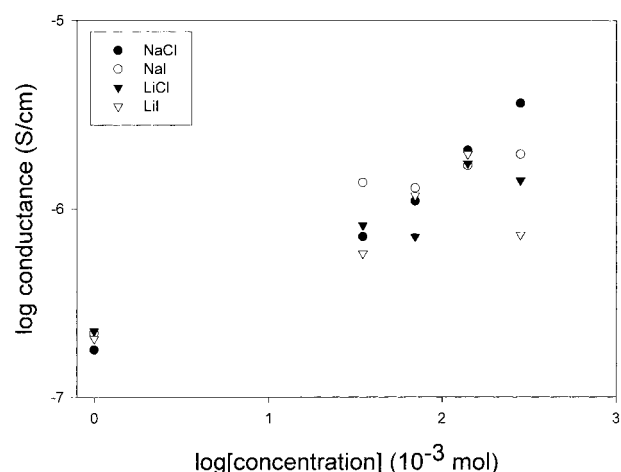


Fig. 2. Effect of M^+X^- molar concentration on the conductance of the starch-based materials.

unit mole, q is the net charge of each species, and μ is the ion mobility of each species. For simplicity, we assume the electronic contribution of the material to the conductance is zero and that ionic mobility is predominant. The amount of moisture in the system can affect the polymer mobility and the ion mobility of the system. However, a statistical analysis of the conductance-concentration plot shows that there is a significant difference at the 95% confidence level in the conductance at higher levels of M^+X^- concentration and rejects moisture content as an independent contribution to conductance (Fig. 2).

Materials were easier to process with higher levels of plasticizer or M^+X^- and could be drawn into thin films. The conductive films were transparent and approximately 0.1 to 0.5 mm thick. Because of the normal variance in mechanical properties of control samples (undoped), normalized mechanical properties are shown

in Fig. 3. Generally, when starch-based materials age, the starch may recrystallize and the material will experience a loss in desirable mechanical properties (reduced elongation and loss of tensile strength). Metal halides apparently functioned as plasticizers in the starch-based solid polymer electrolytes (Fig. 3).

Figure 4 shows that plasticization plays a role in polymer mobility and thus ion mobility. Moderately high ionic conductance was achieved through ion mobility in the starch-based material. In starch-based materials, ion conduction takes place in the amorphous portion of the polymer, probably through a series of transient hydrogen bonds with the hydroxyl groups of the glucopyranosyl rings. Examination of Fig. 4 indicates that there is a 10-fold increase in conductivity with relatively small amounts of M^+X^- . However, there is a point where the addition of M^+X^- does not affect conductance as much as polymer mobility (elongation).

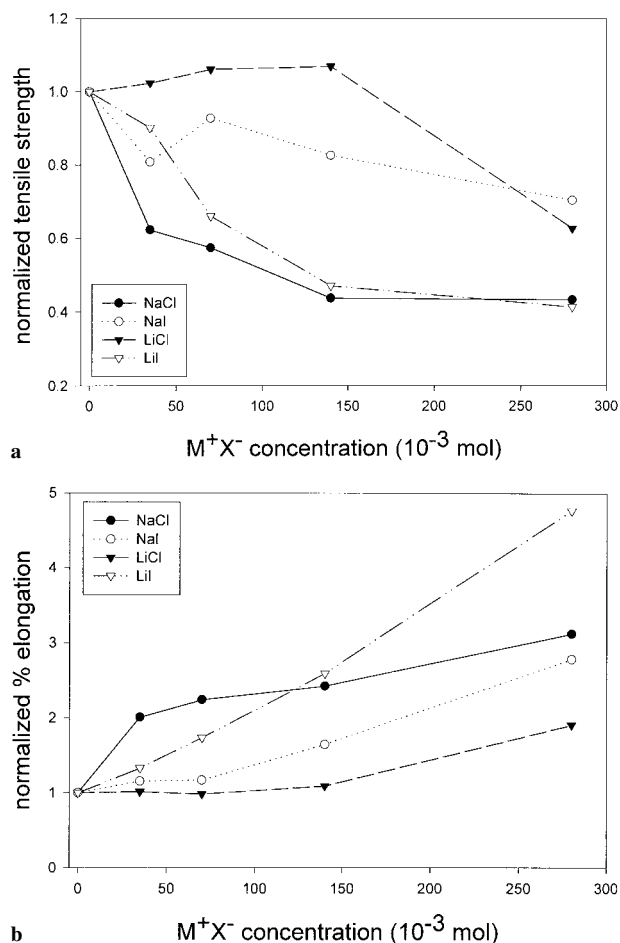


Fig. 3. Mechanical properties of M^+X^- -doped starch-based materials. Tensile strength (a) and elongation (b) are normalized with respect to the control samples in order to directly compare the effects of M^+X^- .

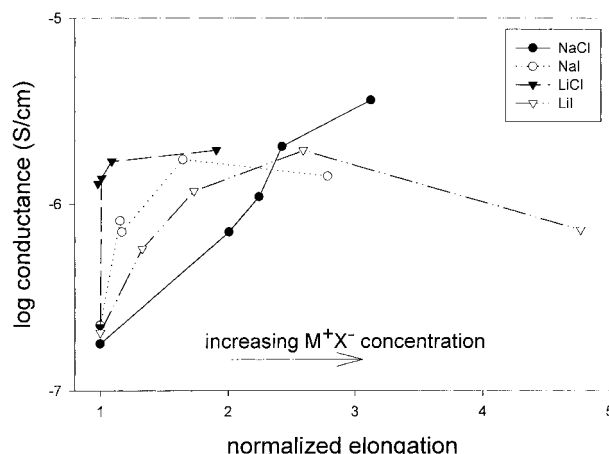


Fig. 4. Starch-based solid polymer electrolytes exhibit increased electrical conductance with increasing M^+X^- content. Greater polymer mobility is exhibited (represented by elongation).

CONCLUSION

Good mechanical properties and moderately high conductivity indicate that starch-based materials can be used for solid polymer electrolytes and can be either intrinsically insulative or a fast ion conductor after doping. While moisture-sensitive, the material properties can be tailored by the addition of metal halides. The increased conductance is due to the addition of M^+X^- ; plasticizers may enhance this effect. Starch-based solid polymer electrolytes may function as biosensors for moisture-sensitive materials, products, or devices. In starch-based solid polymer electrolytes, there is a unique ability to control the molecular matrix and the mass transport properties so that high-performance solid electroactive polymers based on starch can be formulated and fabricated to have moderate conductivity and dimensional stability.

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